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<p>(54) Title: METHOD OF MANUFACTURING OF A DISCRETE ELECTRONIC DEVICE</p>		
<p>(57) Abstract</p> <p>The present invention relates to a method of manufacturing of a discrete electronic device. According to the method, discrete electronic devices are distributed across a surface of a conductor element such that at least some of the contact surfaces of the electronic devices contact the electrodes of the conductor element. In addition, all dimensions of each contact surface of the electronic device are smaller than a width of the gap between the electrodes of the conductor element so that no contact of an electronic device contacts more than one electrode of the conductor element.</p>		

METHOD OF MANUFACTURING OF A DISCRETE ELECTRONIC DEVICE

Related Applications

This application claims priority to provisional applications U.S.S.N. 60/113,523 filed on December 22, 1998.

Field of the Invention

The present invention relates generally to an electronic display and a method of
5 manufacturing an electronic display.

Background of the Invention

Encapsulated, particle-based displays offer a useful means of creating electronic displays. There exist many versions of encapsulated particle-based displays including: encapsulated electrophoretic displays; encapsulated suspended particle displays; and rotating ball displays.

10 Encapsulated, particle-based displays can be made highly reflective, bistable, and optically and electrically efficient. To obtain a high-resolution display, however, individual pixels of a display must be addressable without interference from adjacent pixels. One way to achieve this objective is to provide an array of nonlinear elements, such as diodes where one diode is associated with each pixel. The addressing electrodes are connected to the pixel through
15 the diode.

Most examples of nonlinear elements to date have been fabricated using vacuum-deposited silicon on glass. This process is costly in addition to being complex. The complexity prevents large area devices from being readily constructed. In addition, it is difficult to create silicon transistors on plastic or other flexible film.

20 Several methods of fabricating electrical devices using thin-film fabrication technology and transferring the fabricated devices to another device are known. For example, U.S. Patent No. 5,362,671 describes a lift-off process for fabricating transistors and drive circuitry for a liquid crystal display on a silicon wafer, and then transferring the transistors and drive circuitry

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to an optically transparent substrate to form the display. The liquid crystal display prepared according to this method requires the silicon wafer to undergo a "rubbing" process to align the liquid crystals, which can cause either mechanical or static electric damage to the transistor. Additionally, this transfer process could be used to create flexible active matrix panels, which could be the basis of a film-based liquid crystal panel. Most liquid crystal devices, however, are not readily compatible with flexible substrates, so that displays of this type have not been commercialized.

Another transfer method is commercialized by Alien Technology of Hayward, California. According to this method, discrete circuit elements formed on a silicon wafer are separated from the wafer. The separated circuit elements are dispersed as slurry. The slurry containing the elements is brought in contact with a substrate, which comprises a plurality of indentations. Each indentation is sized and shaped to receive an element in proper orientation. With flow and agitation, the discrete elements fall into the indentations and can form a large area array of discrete elements. Once the discrete elements are bonded to the appropriate conduction lines, the discrete elements can be used to address a display. One problem with this technology, however, is that the size and shape of each indentation must be precise to receive the discrete circuit elements in proper orientation, and therefore can affect yield.

Summary of the Invention

In one aspect, the invention features a method of manufacturing a discrete electronic device. According to the method, a plurality of discrete electronic devices are provided. Each device includes at least one electronic component and at least one contact surface through which an electrical contact can be made with at least one electronic component. A conductor element including a surface bearing at least two electrodes spaced from each other by a gap is provided. The discrete electronic devices are distributed across the surface of the conductor element so that at least some of the contact surfaces of the electronic devices contact the electrodes. All dimensions of each contact surface is smaller than a width of the gap so that no contact surface contacts more than one of the electrodes.

In one embodiment, the discrete electronic devices are provided on a first substrate and the discrete electronic devices are subsequently transferred to a second substrate supporting the

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conductor element. For example, the two electrodes of the conductor element can be pixel electrodes. The second substrate can support a display media and the pixel electrodes, thereby forming a subassembly of an electronic display. Alternatively, the two electrodes can be column electrodes. The first substrate can be a polymer, glass or silicon. In one detailed embodiment, the method further includes the step of separating the discrete electronic device from the first substrate. For example, the discrete electronic devices can be provided on a release layer on the first substrate and the release layer can be etched to separate the electronic devices.

In one embodiment, at least one of the discrete electronic devices can be a two terminal device. The discrete electronic device can have a symmetric current-voltage relationship. The discrete electronic device can be a diode. For example, the discrete electronic device can be a back-to-back diode. Alternatively, the discrete electronic device can be a varistor.

In one embodiment, the discrete electronic devices are provided in a slurry and a coating of the slurry is provided adjacent the surface of the conductor element. The coating can have a thickness less than twice the thickness of each discrete electronic device. The slurry can include conductive particles. For example, the slurry can include gold spheres. The slurry can also include one or all of the following items: an adhesive, a viscosity modifier, a surfactant, a corrosion inhibitor, and a polymer.

In another aspect, the invention features an electrode assembly. The assembly includes a first conductor element, a second conductor element, and a plurality of discrete electronic devices. The first conductor element includes a surface bearing at least two first electrodes spaced from each other by a first gap. The second conductor element is spaced from the surface of the first conductor element. The second conductor element includes a surface bearing at least two second electrodes spaced from each other by a second gap. The electronic devices include at least one electronic component and on opposed sides thereof, first and second contact surfaces through which an electrical contact can be made with the at least one electronic component. The first contact surface of each discrete electronic device is in contact with the surface of the first conductor element. The second contact surface of each discrete electronic device is in contact with the surface of the second conductor element. The dimensions of the first and second contact surfaces is smaller than the width of the first gap and the width of the second gap so that no

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contact surface contacts more than one of the first electrodes on the first conductor element and one of the second electrodes on the second conductor element. The discrete electronic devices are substantially randomly distributed over the surfaces of the first and second conductor elements at a density such that essentially all of the first and second electrodes are in contact with
5 at least one of the discrete electronic devices.

In another aspect, the invention features an electronic display. The display includes a display media, a first conductor element, a second conductor element and a plurality of discrete electronic devices. The first conductor element includes a surface bearing at least two pixel electrodes spaced from each other by a first gap. The second conductor element is spaced from
10 the surface of the first conductor element. The second conductor element includes a surface bearing at least two column electrodes spaced from each other by a second gap. Each electronic device includes at least one electronic component and on opposed sides thereof, first and second contact surfaces through which an electrical contact can be made with the electronic component. The first contact surface of each discrete electronic device is in contact with the surface of the
15 first conductor element. The second contact surface of each discrete electronic device is in contact with the surface of the second conductor element. The dimensions of the first and second contact surfaces is smaller than the width of the gap between adjacent pixel electrodes and the width of the gap between adjacent column electrodes, so that no contact surface contacts more than one of the pixel electrodes and more than one of the column electrodes. The discrete
20 electronic devices are substantially randomly distributed over the surfaces of the first and second conductor elements at a density such that essentially all of the pixel electrodes and the column electrodes are in contact with at least one of the discrete electronic devices.

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Brief Description of the Drawings

The foregoing and other objects, features and advantages of the present invention, as well as the invention itself, will be more fully understood from the following description of preferred embodiments, when read together with the accompanying drawings, in which:

5 Figure 1 shows a cross-section view of an electronic display according to one embodiment of the present invention.

Figure 2 shows a bottom view of an electronic display of Figure 1, with the display media removed.

10 Figure 3a shows a partial cross-section view of an electronic display according to one embodiment of the present invention.

Figure 3b shows a partial cross-section view of an electronic display according to one embodiment of the present invention.

Figure 3c shows a partial cross-section view of an electronic display according to one embodiment of the present invention.

15 Figure 3d shows a partial cross-section view of an electronic display according to one embodiment of the present invention.

Figure 4 illustrates a method of manufacturing an electronic display according to one embodiment of the present invention.

20 Figure 5 illustrates a method of manufacturing an electronic display according to another embodiment of the present invention.

Detailed Description of Preferred Embodiments

Referring to Figure 1, an electronic display 10 includes a substrate 14 supporting an electrode 16, a display medium 12 provided next to the electrode 16, a plurality of pixel electrodes 18 provided next to the display medium 12, a plurality of discrete electronic devices 20 provided next to and in electrical communication with the pixel electrodes 18, and a plurality of column electrodes 22 supported by a substrate 24 provided next to and in electrical

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communication with the discrete electronic devices 20.

The substrate 14 can be made of a transparent material. The substrate 14 can also be a flexible substrate. For example, the substrate 14 can consist of polyester. The electrode 16 can be a common electrode. Alternatively, the electrode 16 can be a plurality of row electrodes. The
5 electrode 16 can consist of a transparent conductive material. For example, an indium tin oxide (ITO), polyaniline or polythiophene coating can be provided on an inner surface 13 of the substrate 14.

The display media 12 can include a plurality of microcapsules 26 dispersed in a binder 28. Each microcapsule 26 can include an electro-optical material. An electro-optical
10 material refers to a material which displays an optical property in response to an electrical signal. Electro-optical material, for example, can be electrophoretic particles or liquid crystals dispersed in a solvent. An electro-optical material can also be bichromal spheres dispersed in a solvent. Details of electro-optical materials within the microcapsules 26 will be discussed further in reference to Figures 3a-3d. An important property of the electro-optical material within the
15 microcapsules 18 is that the material is capable of displaying one visible state upon application of an electric field and a different visual state upon application of a different electric field.

The pixel electrodes 18 can be bonded to the display media 12 through a binder 27. The binder 27, for example, can be a pressure sensitive adhesive. The pixel electrodes 18 can be made from any conductive material. The pixel electrodes 18 can be transparent or opaque. For
20 example, the pixel electrodes 18 can be made from solder paste, copper, copper-clad polyimide, graphite inks, silver inks and other metal containing conductive inks. The pixel electrodes 18 can be formed on a substrate and subsequently bonded to the display media 12. Alternatively, the pixel electrodes 18 can be formed directly on the display media 12. The pixel electrodes 18 can be printed or evaporated. Adjacent pixel electrodes 18a, 18b are spaced apart with a gap (g1)
25 between the two adjacent electrodes 18a, 18b. Each pixel electrode 18 defines a pixel of the display 10.

The discrete electronic devices 20 can be non-linear devices for addressing the pixels of the display 10. The discrete electronic devices 20 can be two terminal devices that have a symmetric current/voltage characteristic, such as back-to-back diodes. In order to ensure that

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each discrete electronic device 20 is electrically connected to no more than one pixel electrode 18, a dimension of the gap (g1) between adjacent pixel electrodes 18a, 18b is larger than any dimension of a contact surface 21 of each discrete electronic device 20. Likewise, a dimension of the gap (g2) between the column electrodes 22 is also larger than any dimension of a contact surface 21 each discrete electronic device 20, as illustrated in Figure 2. For illustration purpose, the display media 12 is not shown in the electronic display 10 of Figure 2. Multiple discrete electronic devices 20 can be connected to a pixel electrode 18. The discrete electronic devices 20 will be discussed in detail with reference to Figures 4 and 5.

The column electrodes 22 can be made of any conductive material, either transparent or opaque. The conductive material can be printed, coated, or vacuum sputtered on a surface 25 of the substrate 24. For example, the column electrodes 22 can also be made using transparent materials such as indium tin oxide and conductive polymers such as polyaniline or polythiophenes. Alternatively, the column electrodes 22 can be made of opaque materials such as solder paste, copper, copper-clad polyimide, graphite inks, silver inks and other metal-containing conductive inks. The substrate 24 can be made of any insulating material, either transparent or opaque. For example, the substrate can be made of polyester.

The architecture of the electronic display 10 shown in Figures 1 and 2 are exemplary only and other architecture for an electronic display may also be used in accordance with this invention.

The display media 12 is now discussed in detail. In one embodiment, the display media 12 comprises a particle-based display media. In one detailed embodiment, the particle-based display media comprises an electronic ink. An electronic ink is an optoelectronically active material which comprises at least two phases: an electrophoretic contrast media phase and a coating/binding phase. The electrophoretic phase comprises, in some embodiments, a single species of electrophoretic particles dispersed in a clear or dyed medium, or more than one species of electrophoretic particles having distinct physical and electrical characteristics dispersed in a clear or dyed medium. In some embodiments the electrophoretic phase is encapsulated, that is, there is a capsule wall phase between the two phases. The coating/binding phase includes, in one embodiment, a polymer matrix that surrounds the electrophoretic phase. In this embodiment, the

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polymer in the polymeric binder is capable of being dried, crosslinked, or otherwise cured as in traditional inks, and therefore a printing process can be used to deposit the electronic ink onto a substrate.

The optical quality of an electronic ink is quite distinct from other electronic display materials. The most notable difference is that the electronic ink provides a high degree of both reflectance and contrast because it is pigment based (as are ordinary printing inks). The light scattered from the electronic ink comes from a very thin layer of pigment close to the top of the viewing surface. In this respect it resembles an ordinary, printed image. Also, electronic ink is easily viewed from a wide range of viewing angles in the same manner as a printed page, and such ink approximates a Lambertian contrast curve more closely than any other electronic display material. Since electronic ink can be printed, it can be included on the same surface with any other printed material, including traditional inks. Electronic ink can be made optically stable in all display configurations, that is, the ink can be set to a persistent optical state. Fabrication of a display by printing an electronic ink is particularly useful in low power applications because of this stability.

Electronic ink displays are novel in that they can be addressed by DC voltages and draw very little current. As such, the conductive leads and electrodes used to deliver the voltage to electronic ink displays can be of relatively high resistivity. The ability to use resistive conductors substantially widens the number and type of materials that can be used as conductors in electronic ink displays. In particular, the use of costly vacuum-sputtered indium tin oxide (ITO) conductors, a standard material in liquid crystal devices, is not required. Aside from cost savings, the replacement of ITO with other materials can provide benefits in appearance, processing capabilities (printed conductors), flexibility, and durability. Additionally, the printed electrodes are in contact only with a solid binder, not with a fluid layer (like liquid crystals). This means that some conductive materials, which would otherwise dissolve or be degraded by contact with liquid crystals, can be used in an electronic ink application. These include opaque metallic inks for the rear electrode (e.g., silver and graphite inks), as well as conductive transparent inks for either substrate. These conductive coatings include conducting or semiconducting colloids, examples of which are indium tin oxide and antimony-doped tin oxide. Organic conductors (polymeric conductors and molecular organic conductors) also may be used.

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Polymers include, but are not limited to, polyaniline and derivatives, polythiophene and derivatives, poly(3,4-ethylenedioxythiophene) (PEDOT) and derivatives, polypyrrole and derivatives, and polyphenylenevinylene (PPV) and derivatives. Organic molecular conductors include, but are not limited to, derivatives of naphthalene, phthalocyanine, and pentacene.

- 5 Polymer layers can be made thinner and more transparent than with traditional displays because conductivity requirements are not as stringent.

Figure 3a shows a cross-section of an electrophoretic display 30 constructed using electronic ink. The binder 32 includes at least one capsule 34, which is filled with a plurality of particles 36 and a dyed suspending fluid 38. In one embodiment, the particles 36 are titania
10 particles. When a direct-current electric field of the appropriate polarity is applied across the capsule 34, the particles 36 move to the viewed surface of the display and scatter light. When the applied electric field is reversed, the particles 36 move to the rear surface of the display and the viewed surface of the display then appears dark.

Figure 3b shows a cross-section of another electrophoretic display 40 constructed using
15 electronic ink. This display comprises a first set of particles 42 and a second set of particles 44 in a capsule 41. The first set of particles 42 and the second set of particles 44 have contrasting optical properties. For example, the first set of particles 42 and the second set of particles 44 can have differing electrophoretic mobilities. In addition, the first set of particles 42 and the second set of particles 44 can have contrasting colors. For example, the first set of particles 42 can be
20 white, while the second set of particles 44 can be black. The capsule 41 further includes a substantially clear fluid. The capsule 41 has electrodes 46 and 46' disposed adjacent it. The electrodes 46, 46' are connected to a source of voltage 48, which may provide an electric field to the capsule 41. In one embodiment, upon application of an electric field across the electrodes 46, 46', the first set of particles 42 move toward electrode 46', while the second set of particles 44
25 move toward electrode 46. In another embodiment, upon application of an electric field across the electrodes 46, 46', the first set of particles 42 move rapidly toward electrode 46', while the second set of particles 44 move only slowly or not at all towards electrode 46, so that the first set of particles packs preferentially at the microcapsule surface adjacent to electrode 46'.

Figure 3c shows a cross-section of a suspended particle display 50. The suspended

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particle display 50 includes needle-like particles 52 in a transparent fluid 54. The particles 52 change their orientation upon application of an AC field across the electrodes 56, 56'. When the AC field is applied, the particles 52 are oriented perpendicular with respect to the display surface and the display appears transparent. When the AC field is removed, the particles 52 are
5 randomly oriented and the display 50 appears opaque.

The electrophoretic and suspended particle displays provided in Figures 3a-3c are exemplary only, and other electrophoretic displays can be used in accordance with the present invention.

In another detailed embodiment, the display media 12 can comprise a plurality of
10 bichromal spheres shown in Figure 4. A bichromal sphere 60 typically comprises a positively charged hemisphere 62 of a first color and a negatively charged hemisphere 64 of a second color in a liquid medium 66. Upon application of an electric field across the sphere 60 through a pair of electrodes 68, 68', the sphere 60 rotates and displays the color of one of the two hemispheres 62, 64.

15 **Materials for Use in Electrophoretic Displays**

Useful materials for constructing the above-described encapsulated electrophoretic displays are discussed in detail below. Many of these materials will be known to those skilled in the art of constructing conventional electrophoretic displays, or those skilled in the art of microencapsulation. The combination of these materials and processes, along with the other
20 necessary components found in an encapsulated electrophoretic display, comprise the invention described herein.

A. Particles

There is much flexibility in the choice of particles for use in electrophoretic displays, as described above. For purposes of this invention, a particle is any component that is charged or
25 capable of acquiring a charge (*i.e.*, has or is capable of acquiring electrophoretic mobility), and, in some cases, this mobility may be zero or close to zero (*i.e.*, the particles will not move). The particles may be neat pigments, dyed (laked) pigments or pigment/polymer composites, or any other component that is charged or capable of acquiring a charge. Typical considerations for the

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electrophoretic particle are its optical properties, electrical properties, and surface chemistry. The particles may be organic or inorganic compounds, and they may either absorb light or scatter light. The particles for use in the invention may further include scattering pigments, absorbing pigments and luminescent particles. The particles may be retroreflective, such as corner cubes, or they may be electroluminescent, such as zinc sulfide particles, which emit light when excited by an AC field, or they may be photoluminescent. Finally, the particles may be surface treated so as to improve charging or interaction with a charging agent, or to improve dispersibility.

A preferred particle for use in electrophoretic displays of the invention is Titania. The titania particles may be coated with a metal oxide, such as aluminum oxide or silicon oxide, for example. The titania particles may have one, two, or more layers of metal-oxide coating. For example, a titania particle for use in electrophoretic displays of the invention may have a coating of aluminum oxide and a coating of silicon oxide. The coatings may be added to the particle in any order.

The electrophoretic particle is usually a pigment, a polymer, a laked pigment, or some combination of the above. A neat pigment can be any pigment, and, usually for a light colored particle, pigments such as, for example, rutile (titania), anatase (titania), barium sulfate, kaolin, or zinc oxide are useful. Some typical particles have high refractive indices, high scattering coefficients, and low absorption coefficients. Other particles are absorptive, such as carbon black or colored pigments used in paints and inks. The pigment should also be insoluble in the suspending fluid. Yellow pigments such as diarylide yellow, hansa yellow, and benzidin yellow have also found use in similar displays. Any other reflective material can be employed for a light colored particle, including non-pigment materials, such as metallic particles.

Useful neat pigments include, but are not limited to, PbCrO₄, Cyan blue GT 55-3295 (American Cyanamid Company, Wayne, NJ), Cibacron Black BG (Ciba Company, Inc., Newport, DE), Cibacron Turquoise Blue G (Ciba), Cibalon Black BGL (Ciba), Orasol Black BRG (Ciba), Orasol Black RBL (Ciba), Acetamine Blac, CBS (E. I. du Pont de Nemours and Company, Inc., Wilmington, DE), Crocein Scarlet N Ex (du Pont) (27290), Fiber Black VF (DuPont) (30235), Luxol Fast Black L (DuPont) (Solv. Black 17), Nirosine Base No. 424 (DuPont) (50415 B), Oil Black BG (DuPont) (Solv. Black 16), Rotalin Black RM (DuPont),

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Sevron Brilliant Red 3 B (DuPont); Basic Black DSC (Dye Specialties, Inc.), Hectolene Black (Dye Specialties, Inc.), Azosol Brilliant Blue B (GAF, Dyestuff and Chemical Division, Wayne, NJ) (Solv. Blue 9), Azosol Brilliant Green BA (GAF) (Solv. Green 2), Azosol Fast Brilliant Red B (GAF), Azosol Fast Orange RA Conc. (GAF) (Solv. Orange 20), Azosol Fast Yellow GRA Conc. (GAF) (13900 A), Basic Black KMPA (GAF), Benzofix Black CW-CF (GAF) (35435),
5 Cellitazol BNFV Ex Soluble CF (GAF) (Disp. Black 9), Celliton Fast Blue AF Ex Conc (GAF) (Disp. Blue 9), Cyper Black IA (GAF) (Basic Blk. 3), Diamine Black CAP Ex Conc (GAF) (30235), Diamond Black EAN Hi Con. CF (GAF) (15710), Diamond Black PBBA Ex (GAF) (16505); Direct Deep Black EA Ex CF (GAF) (30235), Hansa Yellow G (GAF) (11680);
10 Indanthrene Black BBK Powd. (GAF) (59850), Indocarbon CLGS Conc. CF (GAF) (53295), Katigen Deep Black NND Hi Conc. CF (GAF) (15711), Rapidogen Black 3 G (GAF) (Azoic Blk. 4); Sulphone Cyanine Black BA-CF (GAF) (26370), Zambezi Black VD Ex Conc. (GAF) (30015); Rubanox Red CP-1495 (The Sherwin-Williams Company, Cleveland, OH) (15630); Raven 11 (Columbian Carbon Company, Atlanta, GA), (carbon black aggregates with a particle
15 size of about 25 μm), Statex B-12 (Columbian Carbon Co.) (a furnace black of 33 μm average particle size), and chrome green.

Particles may also include laked, or dyed, pigments. Laked pigments are particles that have a dye precipitated on them or which are stained. Lakes are metal salts of readily soluble anionic dyes. These are dyes of azo, triphenylmethane or anthraquinone structure containing one
20 or more sulphonic or carboxylic acid groupings. They are usually precipitated by a calcium, barium or aluminum salt onto a substrate. Typical examples are peacock blue lake (CI Pigment Blue 24) and Persian orange (lake of CI Acid Orange 7), Black M Toner (GAF) (a mixture of carbon black and black dye precipitated on a lake).

A dark particle of the dyed type may be constructed from any light absorbing material,
25 such as carbon black, or inorganic black materials. The dark material may also be selectively absorbing. For example, a dark green pigment may be used. Black particles may also be formed by staining latices with metal oxides, such latex copolymers consisting of any of butadiene, styrene, isoprene, methacrylic acid, methyl methacrylate, acrylonitrile, vinyl chloride, acrylic acid, sodium styrene sulfonate, vinyl acetate, chlorostyrene,
30 dimethylaminopropylmethacrylamide, isocyanoethyl methacrylate and N-

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(isobutoxymethacrylamide), and optionally including conjugated diene compounds such as diacrylate, triacrylate, dimethylacrylate and trimethacrylate. Black particles may also be formed by a dispersion polymerization technique.

In the systems containing pigments and polymers, the pigments and polymers may form multiple domains within the electrophoretic particle, or be aggregates of smaller pigment/polymer combined particles. Alternatively, a central pigment core may be surrounded by a polymer shell. The pigment, polymer, or both can contain a dye. The optical purpose of the particle may be to scatter light, absorb light, or both. Useful sizes may range from 1 nm up to about 100 μm , as long as the particles are smaller than the bounding capsule. In a preferred embodiment, the density of the electrophoretic particle may be substantially matched to that of the suspending (*i.e.*, electrophoretic) fluid. As defined herein, a suspending fluid has a density that is "substantially matched" to the density of the particle if the difference in their respective densities is between about zero and about two g/ml. This difference is preferably between about zero and about 0.5 g/ml.

Useful polymers for the particles include, but are not limited to: polystyrene, polyethylene, polypropylene, phenolic resins, Du Pont Elvax resins (ethylene-vinyl acetate copolymers), polyesters, polyacrylates, polymethacrylates, ethylene acrylic acid or methacrylic acid copolymers (Nucel Resins - DuPont, Primacor Resins- Dow Chemical), acrylic copolymers and terpolymers (Elvacite Resins, DuPont) and PMMA. Useful materials for homopolymer / pigment phase separation in high shear melt include, but are not limited to, polyethylene, polypropylene, polymethylmethacrylate, polyisobutylmethacrylate, polystyrene, polybutadiene, polyisoprene, polyisobutylene, polylauryl methacrylate, polystearyl methacrylate, polyisobornyl methacrylate, poly-t-butyl methacrylate, polyethyl methacrylate, polymethyl acrylate, polyethyl acrylate, polyacrylonitrile, and copolymers of two or more of these materials. Some useful pigment/polymer complexes that are commercially available include, but are not limited to, Process Magenta PM 1776 (Magruder Color Company, Inc., Elizabeth, NJ), Methyl Violet PMA VM6223 (Magruder Color Company, Inc., Elizabeth, NJ), and Naphthol FGR RF6257 (Magruder Color Company, Inc., Elizabeth, NJ).

The pigment-polymer composite may be formed by a physical process, (*e.g.*, attrition or

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ball milling), a chemical process (*e.g.*, microencapsulation or dispersion polymerization), or any other process known in the art of particle production. From the following non-limiting examples, it may be seen that the processes and materials for both the fabrication of particles and the charging thereof are generally derived from the art of liquid toner, or liquid immersion development. Thus any of the known processes from liquid development are particularly, but not exclusively, relevant.

New and useful electrophoretic particles may still be discovered, but a number of particles already known to those skilled in the art of electrophoretic displays and liquid toners can also prove useful. In general, the polymer requirements for liquid toners and encapsulated electrophoretic inks are similar, in that the pigment or dye must be easily incorporated therein, either by a physical, chemical, or physicochemical process, may aid in the colloidal stability, and may contain charging sites or may be able to incorporate materials which contain charging sites. One general requirement from the liquid toner industry that is not shared by encapsulated electrophoretic inks is that the toner must be capable of "fixing" the image, *i.e.*, heat fusing together to create a uniform film after the deposition of the toner particles.

Typical manufacturing techniques for particles are drawn from the liquid toner and other arts and include ball milling, attrition, jet milling, *etc.* The process will be illustrated for the case of a pigmented polymeric particle. In such a case the pigment is compounded in the polymer, usually in some kind of high shear mechanism such as a screw extruder. The composite material is then (wet or dry) ground to a starting size of around 10 μm . It is then dispersed in a carrier liquid, for example ISOPAR[®] (Exxon, Houston, TX), optionally with some charge control agent(s), and milled under high shear for several hours down to a final particle size and/or size distribution.

Another manufacturing technique for particles drawn from the liquid toner field is to add the polymer, pigment, and suspending fluid to a media mill. The mill is started and simultaneously heated to temperature at which the polymer swells substantially with the solvent. This temperature is typically near 100°C. In this state, the pigment is easily encapsulated into the swollen polymer. After a suitable time, typically a few hours, the mill is gradually cooled back to ambient temperature while stirring. The milling may be continued for some time to

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achieve a small enough particle size, typically a few microns in diameter. The charging agents may be added at this time. Optionally, more suspending fluid may be added.

Chemical processes such as dispersion polymerization, mini- or micro-emulsion polymerization, suspension polymerization precipitation, phase separation, solvent evaporation, *in situ* polymerization, seeded emulsion polymerization, or any process which falls under the general category of microencapsulation may be used. A typical process of this type is a phase separation process wherein a dissolved polymeric material is precipitated out of solution onto a dispersed pigment surface through solvent dilution, evaporation, or a thermal change. Other processes include chemical means for staining polymeric latices, for example with metal oxides or dyes.

B. Suspending Fluid

The suspending fluid containing the particles can be chosen based on properties such as density, refractive index, and solubility. A preferred suspending fluid has a low dielectric constant (about 2), high volume resistivity (about 10^{15} ohm-cm), low viscosity (less than 5 cst), low toxicity and environmental impact, low water solubility (less than 10 ppm), high specific gravity (greater than 1.5), a high boiling point (greater than 90°C), and a low refractive index (less than 1.2).

The choice of suspending fluid may be based on concerns of chemical inertness, density matching to the electrophoretic particle, or chemical compatibility with both the electrophoretic particle and bounding capsule. The viscosity of the fluid should be low when you want the particles to move. The refractive index of the suspending fluid may also be substantially matched to that of the particles. As used herein, the refractive index of a suspending fluid "is substantially matched" to that of a particle if the difference between their respective refractive indices is between about zero and about 0.3, and is preferably between about 0.05 and about 0.2.

Additionally, the fluid may be chosen to be a poor solvent for some polymers, which is advantageous for use in the fabrication of microparticles because it increases the range of polymeric materials useful in fabricating particles of polymers and pigments. Organic solvents, such as halogenated organic solvents, saturated linear or branched hydrocarbons, silicone oils,

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and low molecular weight halogen-containing polymers are some useful suspending fluids. The suspending fluid may comprise a single fluid. The fluid will, however, often be a blend of more than one fluid in order to tune its chemical and physical properties. Furthermore, the fluid may contain surface modifiers to modify the surface energy or charge of the electrophoretic particle or bounding capsule. Reactants or solvents for the microencapsulation process (oil soluble monomers, for example) can also be contained in the suspending fluid. Charge control agents can also be added to the suspending fluid.

Useful organic solvents include, but are not limited to, epoxides, such as, for example, decane epoxide and dodecane epoxide; vinyl ethers, such as, for example, cyclohexyl vinyl ether and Decave® (International Flavors & Fragrances, Inc., New York, NY); and aromatic hydrocarbons, such as, for example, toluene and naphthalene. Useful halogenated organic solvents include, but are not limited to, tetrafluorodibromoethylene, tetrachloroethylene, trifluorochloroethylene, 1,2,4-trichlorobenzene, carbon tetrachloride. These materials have high densities. Useful hydrocarbons include, but are not limited to, dodecane, tetradecane, the aliphatic hydrocarbons in the Isopar® series (Exxon, Houston, TX), Norpar® (series of normal paraffinic liquids), Shell-Sol® (Shell, Houston, TX), and Sol-Trol® (Shell), naphtha, and other petroleum solvents. These materials usually have low densities. Useful examples of silicone oils include, but are not limited to, octamethyl cyclosiloxane and higher molecular weight cyclic siloxanes, poly (methyl phenyl siloxane), hexamethyldisiloxane, and polydimethylsiloxane. These materials usually have low densities. Useful low molecular weight halogen-containing polymers include, but are not limited to, poly(chlorotrifluoroethylene) polymer (Halogenated hydrocarbon Inc., River Edge, NJ), Galden® (a perfluorinated ether from Ausimont, Morristown, NJ), or Krytox® from DuPont (Wilmington, DE). In a preferred embodiment, the suspending fluid is a poly(chlorotrifluoroethylene) polymer. In a particularly preferred embodiment, this polymer has a degree of polymerization from about 2 to about 10. Many of the above materials are available in a range of viscosities, densities, and boiling points.

The fluid must be capable of being formed into small droplets prior to a capsule being formed. Processes for forming small droplets include flow-through jets, membranes, nozzles, or orifices, as well as shear-based emulsifying schemes. The formation of small drops may be assisted by electrical or sonic fields. Surfactants and polymers can be used to aid in the

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stabilization and emulsification of the droplets in the case of an emulsion type encapsulation. A preferred surfactant for use in displays of the invention is sodium dodecylsulfate.

It can be advantageous in some displays for the suspending fluid to contain an optically absorbing dye. This dye must be soluble in the fluid, but will generally be insoluble in the other components of the capsule. There is much flexibility in the choice of dye material. The dye can be a pure compound, or blends of dyes to achieve a particular color, including black. The dyes can be fluorescent, which would produce a display in which the fluorescence properties depend on the position of the particles. The dyes can be photoactive, changing to another color or becoming colorless upon irradiation with either visible or ultraviolet light, providing another means for obtaining an optical response. Dyes could also be polymerizable, forming a solid absorbing polymer inside the bounding shell.

There are many dyes that can be chosen for use in encapsulated electrophoretic display. Properties important here include light fastness, solubility in the suspending liquid, color, and cost. These are generally from the class of azo, anthraquinone, and triphenylmethane type dyes and may be chemically modified so as to increase the solubility in the oil phase and reduce the adsorption by the particle surface.

A number of dyes already known to those skilled in the art of electrophoretic displays will prove useful. Useful azo dyes include, but are not limited to: the Oil Red dyes, and the Sudan Red and Sudan Black series of dyes. Useful anthraquinone dyes include, but are not limited to: the Oil Blue dyes, and the Macrolex Blue series of dyes. Useful triphenylmethane dyes include, but are not limited to, Michler's hydrol, Malachite Green, Crystal Violet, and Auramine O.

C. Charge Control Agents and Particle Stabilizers

Charge control agents are used to provide good electrophoretic mobility to the electrophoretic particles. Stabilizers are used to prevent agglomeration of the electrophoretic particles, as well as prevent the electrophoretic particles from irreversibly depositing onto the capsule wall. Either component can be constructed from materials across a wide range of molecular weights (low molecular weight, oligomeric, or polymeric), and may be pure or a

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mixture. In particular, suitable charge control agents are generally adapted from the liquid toner art. The charge control agent used to modify and/or stabilize the particle surface charge is applied as generally known in the arts of liquid toners, electrophoretic displays, non-aqueous paint dispersions, and engine-oil additives. In all of these arts, charging species may be added to non-aqueous media in order to increase electrophoretic mobility or increase electrostatic stabilization. The materials can improve steric stabilization as well. Different theories of charging are postulated, including selective ion adsorption, proton transfer, and contact electrification.

An optional charge control agent or charge director may be used. These constituents typically consist of low molecular weight surfactants, polymeric agents, or blends of one or more components and serve to stabilize or otherwise modify the sign and/or magnitude of the charge on the electrophoretic particles. The charging properties of the pigment itself may be accounted for by taking into account the acidic or basic surface properties of the pigment, or the charging sites may take place on the carrier resin surface (if present), or a combination of the two. Additional pigment properties which may be relevant are the particle size distribution, the chemical composition, and the lightfastness. The charge control agent used to modify and/or stabilize the particle surface charge is applied as generally known in the arts of liquid toners, electrophoretic displays, non-aqueous paint dispersions, and engine-oil additives. In all of these arts, charging species may be added to non-aqueous media in order to increase electrophoretic mobility or increase electrostatic stabilization. The materials can improve steric stabilization as well. Different theories of charging are postulated, including selective ion adsorption, proton transfer, and contact electrification.

Charge adjuvants may also be added. These materials increase the effectiveness of the charge control agents or charge directors. The charge adjuvant may be a polyhydroxy compound or an aminoalcohol compound, which are preferably soluble in the suspending fluid in an amount of at least 2% by weight. Examples of polyhydroxy compounds which contain at least two hydroxyl groups include, but are not limited to, ethylene glycol, 2,4,7,9-tetramethyl-decane-4,7-diol, poly(propylene glycol), pentaethylene glycol, tripropylene glycol, triethylene glycol, glycerol, pentaerythritol, glycerol tris(12 hydroxystearate), propylene glycerol monohydroxystearate, and ethylene glycol monohydroxystearate. Examples of aminoalcohol

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compounds which contain at least one alcohol function and one amine function in the same molecule include, but are not limited to, triisopropanolamine, triethanolamine, ethanolamine, 3-amino-1-propanol, o-aminophenol, 5-amino-1-pentanol, and tetrakis(2-hydroxyethyl)ethylene-diamine. The charge adjuvant is preferably present in the suspending fluid in an amount of about
5 1 to about 100 mg/g of the particle mass, and more preferably about 50 to about 200 mg/g.

The surface of the particle may also be chemically modified to aid dispersion, to improve surface charge, and to improve the stability of the dispersion, for example. Surface modifiers include organic siloxanes, organohalogen silanes and other functional silane coupling agents (Dow Corning® Z-6070, Z-6124, and 3 additive, Midland, MI); organic titanates and zirconates
10 (Tyzor® TOT, TBT, and TE Series, DuPont, Wilmington, DE); hydrophobing agents, such as long chain (C12 to C50) alkyl and alkyl benzene sulphonic acids, fatty amines or diamines and their salts or quarternary derivatives; and amphipathic polymers which can be covalently bonded to the particle surface.

In general, it is believed that charging results as an acid-base reaction between some
15 moiety present in the continuous phase and the particle surface. Thus useful materials are those which are capable of participating in such a reaction, or any other charging reaction as known in the art.

Different non-limiting classes of charge control agents which are useful include organic sulfates or sulfonates, metal soaps, block or comb copolymers, organic amides, organic
20 zwitterions, and organic phosphates and phosphonates. Useful organic sulfates and sulfonates include, but are not limited to, sodium bis(2-ethyl hexyl) sulfosuccinate, calcium dodecyl benzene sulfonate, calcium petroleum sulfonate, neutral or basic barium dinonylnaphthalene sulfonate, neutral or basic calcium dinonylnaphthalene sulfonate, dodecylbenzenesulfonic acid sodium salt, and ammonium lauryl sulphate. Useful metal soaps include, but are not limited to,
25 basic or neutral barium petronate, calcium petronate, Co-, Ca-, Cu-, Mn-, Ni-, Zn-, and Fe- salts of naphthenic acid, Ba-, Al-, Zn-, Cu-, Pb-, and Fe- salts of stearic acid, divalent and trivalent metal carboxylates, such as aluminum tristearate, aluminum octoanate, lithium heptanoate, iron stearate, iron distearate, barium stearate, chromium stearate, magnesium octanoate, calcium stearate, iron naphthenate, and zinc naphthenate, Mn- and Zn- heptanoate, and Ba-, Al-, Co-,

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Mn-, and Zn- octanoate. Useful block or comb copolymers include, but are not limited to, AB diblock copolymers of (A) polymers of 2-(N,N)-dimethylaminoethyl methacrylate quaternized with methyl-p-toluenesulfonate and (B) poly-2-ethylhexyl methacrylate, and comb graft copolymers with oil soluble tails of poly (12-hydroxystearic acid) and having a molecular weight of about 1800, pendant on an oil-soluble anchor group of poly (methyl methacrylate-methacrylic acid). Useful organic amides include, but are not limited to, polyisobutylene succinimides such as OLOA 1200, and N-vinyl pyrrolidone polymers. Useful organic zwitterions include, but are not limited to, lecithin. Useful organic phosphates and phosphonates include, but are not limited to, the sodium salts of phosphated mono- and di-glycerides with saturated and unsaturated acid substituents.

Particle dispersion stabilizers may be added to prevent particle flocculation or attachment to the capsule walls. For the typical high resistivity liquids used as suspending fluids in electrophoretic displays, nonaqueous surfactants may be used. These include, but are not limited to, glycol ethers, acetylenic glycols, alkanolamides, sorbitol derivatives, alkyl amines, quaternary amines, imidazolines, dialkyl oxides, and sulfosuccinates.

D. Encapsulation

There is a long and rich history to encapsulation, with numerous processes and polymers having proven useful in creating capsules. Encapsulation of the internal phase may be accomplished in a number of different ways. Numerous suitable procedures for microencapsulation are detailed in both *Microencapsulation, Processes and Applications*, (I. E. Vandegaer, ed.), Plenum Press, New York, NY (1974) and Gutcho, *Microcapsules and Microencapsulation Techniques*, Nuyes Data Corp., Park Ridge, N.J. (1976). The processes fall into several general categories, all of which can be applied to the present invention: interfacial polymerization, *in situ* polymerization, physical processes, such as coextrusion and other phase separation processes, in-liquid curing, and simple/complex coacervation.

Numerous materials and processes should prove useful in formulating displays of the present invention. Useful materials for simple coacervation processes include, but are not limited to, gelatin, polyvinyl alcohol, polyvinyl acetate, and cellulosic derivatives, such as, for

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example, carboxymethylcellulose. Useful materials for complex coacervation processes include, but are not limited to, gelatin, acacia, carageenan, carboxymethylcellulose, hydrolyzed styrene anhydride copolymers, agar, alginate, casein, albumin, methyl vinyl ether co-maleic anhydride, and cellulose phthalate. Useful materials for phase separation processes include, but are not limited to, polystyrene, PMMA, polyethyl methacrylate, polybutyl methacrylate, ethyl cellulose, polyvinyl pyridine, and poly acrylonitrile. Useful materials for *in situ* polymerization processes include, but are not limited to, polyhydroxyamides, with aldehydes, melamine, or urea and formaldehyde; water-soluble oligomers of the condensate of melamine, or urea and formaldehyde; and vinyl monomers, such as, for example, styrene, MMA and acrylonitrile.

Finally, useful materials for interfacial polymerization processes include, but are not limited to, diacyl chlorides, such as, for example, sebacoyl, adipoyl, and di- or poly- amines or alcohols, and isocyanates. Useful emulsion polymerization materials may include, but are not limited to, styrene, vinyl acetate, acrylic acid, butyl acrylate, t-butyl acrylate, methyl methacrylate, and butyl methacrylate.

Capsules produced may be dispersed into a curable carrier, resulting in an ink which may be printed or coated on large and arbitrarily shaped or curved surfaces using conventional printing and coating techniques.

In the context of the present invention, one skilled in the art will select an encapsulation procedure and wall material based on the desired capsule properties. These properties include the distribution of capsule radii; electrical, mechanical, diffusion, and optical properties of the capsule wall; and chemical compatibility with the internal phase of the capsule.

The capsule wall generally has a high electrical resistivity. Although it is possible to use walls with relatively low resistivities, this may limit performance in requiring relatively higher addressing voltages. The capsule wall should also be mechanically strong (although if the finished capsule powder is to be dispersed in a curable polymeric binder for coating, mechanical strength is not as critical). The capsule wall should generally not be porous. If, however, it is desired to use an encapsulation procedure that produces porous capsules, these can be overcoated in a post-processing step (*i.e.*, a second encapsulation). Moreover, if the capsules are to be dispersed in a curable binder, the binder will serve to close the pores. The capsule walls should

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be optically clear. The wall material may, however, be chosen to match the refractive index of the internal phase of the capsule (*i.e.*, the suspending fluid) or a binder in which the capsules are to be dispersed. For some applications (*e.g.*, interposition between two fixed electrodes), monodispersed capsule radii are desirable.

5 An encapsulation procedure involves a polymerization between urea and formaldehyde in an aqueous phase of an oil/water emulsion in the presence of a negatively charged, carboxyl-substituted, linear hydrocarbon polyelectrolyte material. The resulting capsule wall is a urea/formaldehyde copolymer, which discretely encloses the internal phase. The capsule is clear, mechanically strong, and has good resistivity properties.

10 The related technique of *in situ* polymerization utilizes an oil/water emulsion, which is formed by dispersing the electrophoretic composition (*i.e.*, the dielectric liquid containing a suspension of the pigment particles) in an aqueous environment. The monomers polymerize to form a polymer with higher affinity for the internal phase than for the aqueous phase, thus condensing around the emulsified oily droplets. In one especially useful *in situ* polymerization
15 processes, urea and formaldehyde condense in the presence of poly(acrylic acid) (See, *e.g.*, U.S. Patent No. 4,001,140). In other useful process, any of a variety of cross-linking agents borne in aqueous solution is deposited around microscopic oil droplets. Such cross-linking agents include aldehydes, especially formaldehyde, glyoxal, or glutaraldehyde; alum; zirconium salts; and poly isocyanates. The entire disclosures of the 4,001,140 and 4,273,672 patents are hereby
20 incorporated by reference herein.

 The coacervation approach also utilizes an oil/water emulsion. One or more colloids are coacervated (*i.e.*, agglomerated) out of the aqueous phase and deposited as shells around the oily droplets through control of temperature, pH and/or relative concentrations, thereby creating the microcapsule. Materials suitable for coacervation include gelatins and gum arabic.

25 The interfacial polymerization approach relies on the presence of an oil-soluble monomer in the electrophoretic composition, which once again is present as an emulsion in an aqueous phase. The monomers in the minute hydrophobic droplets react with a monomer introduced into the aqueous phase, polymerizing at the interface between the droplets and the surrounding aqueous medium and forming shells around the droplets. Although the resulting walls are
30 relatively thin and may be permeable, this process does not require the elevated temperatures

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characteristic of some other processes, and therefore affords greater flexibility in terms of choosing the dielectric liquid.

Coating aids can be used to improve the uniformity and quality of the coated or printed electrophoretic ink material. Wetting agents are typically added to adjust the interfacial tension at the coating/substrate interface and to adjust the liquid/air surface tension. Wetting agents include, but are not limited to, anionic and cationic surfactants, and nonionic species, such as silicone or fluoropolymer based materials. Dispersing agents may be used to modify the interfacial tension between the capsules and binder, providing control over flocculation and particle settling.

Surface tension modifiers can be added to adjust the air/ink interfacial tension. Polysiloxanes are typically used in such an application to improve surface leveling while minimizing other defects within the coating. Surface tension modifiers include, but are not limited to, fluorinated surfactants, such as, for example, the Zonyl® series from DuPont (Wilmington, DE), the Fluorod® series from 3M (St. Paul, MN), and the fluoroalkyl series from Autochem (Glen Rock, NJ); siloxanes, such as, for example, Silwet® from Union Carbide (Danbury, CT); and polyethoxy and polypropoxy alcohols. Antifoams, such as silicone and silicone-free polymeric materials, may be added to enhance the movement of air from within the ink to the surface and to facilitate the rupture of bubbles at the coating surface. Other useful antifoams include, but are not limited to, glyceryl esters, polyhydric alcohols, compounded antifoams, such as oil solutions of alkyl benzenes, natural fats, fatty acids, and metallic soaps, and silicone antifoaming agents made from the combination of dimethyl siloxane polymers and silica. Stabilizers such as uv-absorbers and antioxidants may also be added to improve the lifetime of the ink.

Other additives to control properties like coating viscosity and foaming can also be used in the coating fluid. Stabilizers (UV-absorbers, antioxidants) and other additives which could prove useful in practical materials.

E. Binder Material

The binder is used as a non-conducting, adhesive medium supporting and protecting the

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capsules, as well as binding the electrode materials to the capsule dispersion. Binders are available in many forms and chemical types. Among these are water-soluble polymers, water-borne polymers, oil-soluble polymers, thermoset and thermoplastic polymers, and radiation-cured polymers.

- 5 Among the water-soluble polymers are the various polysaccharides, the polyvinyl alcohols, N-methylpyrrolidone, N-vinylpyrrolidone, the various Carbowax® species (Union Carbide, Danbury, CT), and poly-2-hydroxyethylacrylate.

- The water-dispersed or water-borne systems are generally latex compositions, typified by the Neorez® and Neocryl® resins (Zeneca Resins, Wilmington, MA), Acrysol® (Rohm and Haas, Philadelphia, PA), Bayhydrol® (Bayer, Pittsburgh, PA), and the Cytec Industries (West Paterson, NJ) HP line. These are generally latices of polyurethanes, occasionally compounded with one or more of the acrylics, polyesters, polycarbonates or silicones, each lending the final cured resin in a specific set of properties defined by glass transition temperature, degree of "tack," softness, clarity, flexibility, water permeability and solvent resistance, elongation modulus and tensile strength, thermoplastic flow, and solids level. Some water-borne systems can be mixed with reactive monomers and catalyzed to form more complex resins. Some can be further cross-linked by the use of a crosslinking reagent, such as an aziridine, for example, which reacts with carboxyl groups.

- A typical application of a water-borne resin and aqueous capsules follows. A volume of particles is centrifuged at low speed to separate excess water. After a given centrifugation process, for example 10 minutes at 60 x G, the capsules are found at the bottom of the centrifuge tube, while the water portion is at the top. The water portion is carefully removed (by decanting or pipetting). The mass of the remaining capsules is measured, and a mass of resin is added such that the mass of resin is between one eighth and one tenth of the weight of the capsules. This mixture is gently mixed on an oscillating mixer for approximately one half hour. After about one half hour, the mixture is ready to be coated onto the appropriate substrate.

 The thermoset systems are exemplified by the family of epoxies. These binary systems can vary greatly in viscosity, and the reactivity of the pair determines the "pot life" of the mixture. If the pot life is long enough to allow a coating operation, capsules may be coated in an

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ordered arrangement in a coating process prior to the resin curing and hardening.

Thermoplastic polymers, which are often polyesters, are molten at high temperatures. A typical application of this type of product is hot-melt glue. A dispersion of heat-resistant capsules could be coated in such a medium. The solidification process begins during cooling,
5 and the final hardness, clarity and flexibility are affected by the branching and molecular weight of the polymer.

Oil or solvent-soluble polymers are often similar in composition to the water-borne system, with the obvious exception of the water itself. The latitude in formulation for solvent systems is enormous, limited only by solvent choices and polymer solubility. Of considerable
10 concern in solvent-based systems is the viability of the capsule itself - the integrity of the capsule wall cannot be compromised in any way by the solvent.

Radiation cure resins are generally found among the solvent-based systems. Capsules may be dispersed in such a medium and coated, and the resin may then be cured by a timed exposure to a threshold level of ultraviolet radiation, either long or short wavelength. As in all
15 cases of curing polymer resins, final properties are determined by the branching and molecular weights of the monomers, oligomers and crosslinkers.

A number of "water-reducible" monomers and oligomers are, however, marketed. In the strictest sense, they are not water soluble, but water is an acceptable diluent at low concentrations and can be dispersed relatively easily in the mixture. Under these circumstances, water is used to
20 reduce the viscosity (initially from thousands to hundreds of thousands centipoise). Water-based capsules, such as those made from a protein or polysaccharide material, for example, could be dispersed in such a medium and coated, provided the viscosity could be sufficiently lowered. Curing in such systems is generally by ultraviolet radiation.

According to the present invention, an electronic display is prepared by fabricating the
25 discrete electronic devices using a thin-film fabrication technology or another processing technology and subsequently transferring the fabricated discrete electronic devices to an encapsulated display media. As used herein, the term "thin-film technology" refers to one or more layers of semiconducting materials, deposited in layers less than about one micron in

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thickness.

Referring to Figure 4, the discrete electronic devices 80 are fabricated on a substrate 82 (step 10). The electronic devices can be non-linear devices for addressing the display. The non-linear electronic devices can be two terminal devices. Each discrete electronic device 80 has
5 a first contact surface 81 on one side of the discrete electronic device 80 and a second contact surface 83 on the other side of the discrete electronic device 80, opposite the first contact surface 81 in symmetry. Either the first contact surface 81 or the second contact surface 83 can come in contact with the pixel electrodes 18. This geometry precludes the need to orient the discrete electronic devices 80 when bringing them in contact with electrodes. For example, the non-
10 linear electronic device 80 can be back-to-back diodes. In one embodiment, each back-to-back diode has a P-N-P layer structure. In another embodiment, each back-to-back diode has an N-P-N layer structure.

The substrate 82 can be a silicon wafer. Alternatively, the substrate 82 can be a glass or polymer substrate. In one embodiment, a release layer 84 is provided on the substrate 82 and the
15 discrete electronic devices 80 are provided on the release layer 84. The release layer 84 allows the discrete electronic devices 80 to be separated from the substrate 82 subsequent to their fabrication by etching away the release layer 84.

In one embodiment, the discrete electronic devices 80 are fabricated using a conventional microfabrication technique such as deposition, evaporation, and photo-lithography. These
20 techniques are well known to those skilled in the art. Alternatively, the discrete electronic devices 80 can be printed. The term printing is used to include all forms of printing and coating, including without limitation: premetered coatings such as patch die coating, slot or extension coating, slide or cascade coating, and curtain coating, roll coating such as knife over roll coating, meniscus coating, spin coating, brush coating, thermal printing, ink-jet printing and other similar
25 techniques. For example, an organic semiconductor material can be printed on the substrate 82 to form the electronic device 80. The semiconductor material can be an organic polymer. In one embodiment, the organic semiconductor comprises a polymeric or oligomeric semiconductor. Examples of suitable polymeric semiconductors include, but are not limited to, polythiophene, poly(3-alkyl), alkyl-substituted oligothiophene, polythienylenevinylene, poly(para-

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phenylenevinylene) and doped versions of these polymers. An example of suitable oligomeric semiconductor is alpha-hexathienylene.

In another embodiment, the organic semiconductor material comprises a carbon based compound. Examples of suitable carbon based compounds include, but are not limited to,
5 pentacene, phthalocyanine, benzodithiophene, fullerene, buckminsterfullerene, tetracyanonaphthoquinone, and tetrakis(methylamino)ethylene.

The fabricated discrete electronic devices 80 are separated from each other and from the substrate 82 (step 20). In the embodiment of Figure 4, the electronic devices 80 are fabricated on a release layer 84, which is etched away to separate the electronic devices 80. Alternatively, the
10 discrete electronic devices 80 can be mechanically separated from the substrate 82.

The separated discrete electronic devices 80 are provided in a solution to form a slurry (step 30). The slurry 86 can include a liquid carrier. The slurry 98 can also include a polymer. The slurry 98 can include any or all of the following items: a viscosity modifier, a surfactant, and a corrosion inhibitor. Examples of suitable viscosity modifiers include, but are not limited to,
15 polyisobutylene, copolymers of ethylene and propylene and higher alpha-olefins, polymethacrylates, polyalkylmethacrylates, methacrylate copolymers, copolymers of an unsaturated dicarboxylic acid and a vinyl compound, inter polymers of styrene and acrylic esters, and partially hydrogenated copolymers of styrene/isoprene, styrene/butadiene, and isoprene/butadiene, as well as the partially hydrogenated homopolymers of butadiene and
20 isoprene and isoprene/divinylbenzene. Examples of suitable surfactants include, but are not limited to, fluorinated surfactants, such as, for example, the Zonyl ® series from DuPont (Wilmington, DE), the Fluorod ® series from 3M (St. Paul, MN), and the fluoroalkyl series from Autochem (Glen Rock, NJ); siloxanes, such as, for example, Silwet ® from Union Carbide (Danbury, CT); and polyethoxy and polypropoxy alcohols. Examples of suitable corrosion
25 inhibitors include but are not limited to nitrogenous compounds such as imines, benzothirazoles and benzoimidazoles. U.S. Patent No. 5,951,918, incorporated herein by reference, provides other examples of corrosive inhibitors. The slurry 86 can also include a binder. Examples of suitable binders include but are not limited to water soluble polymers such as polysaccharides and polyvinyl alcohols, water-borne systems such as Neotez® and Neocryl® resins (Zeneca

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Resino, Wilmington, MA), thermoset systems such as epoxies and thermoplastic polymers such as polyesters. The slurry 86 can further include conductive particles such as gold spheres to enhance electrical contact. In one embodiment, the slurry 86 includes an anisotropic conductive film such as z-axis adhesive film nos. 5303 and 7303 available from 3M (St. Paul, MN).

5 A subassembly comprising a substrate 14 supporting an electrode 16, a display media 12, and a plurality of pixel electrodes 18 is provided. The slurry 86 is provided on the subassembly next to the pixel electrodes 18 to form a coating having a thickness less than twice the thickness (t) of the discrete electronic devices 80. This thickness limitation of the coating prevents multiple discrete electronic devices 80 from overlapping over a single pixel electrode 18. This
10 thickness limitation of the coating also allows the discrete electronic devices 80 to be oriented horizontally, not vertically, with respect to the pixel electrodes 18 as shown in step 40. Since the dimension of the contact surfaces 81, 83 is less than the gap (g1) between the pixel electrodes 18, an electronic device 80 does not contact more than one pixel electrode 18. In one embodiment, a pressure is applied during step 40 to ensure that the discrete electronic devices 80 are in good
15 electrical contact with the pixel electrodes 18. In another embodiment, in which the slurry 86 includes a polymeric material, heat can be applied prior to applying the pressure in order to displace the polymeric material between the electronic devices 80 and the pixel electrodes 18.

Thereafter, a circuit layer (not shown) comprising a plurality of column electrodes can be bonded to the electronic devices 80. In one embodiment, an adhesive layer is provided between
20 the discrete electronic devices and the column electrodes. The adhesive layer, for example, can be Double Coated Film Tape Nos. 9443, 443, and 444 available from 3M Company (St. Paul, MN).

In another embodiment, an electronic display is fabricated according to the process illustrated in Figure 5. Discrete electronic devices 80 are prepared on a substrate 82 as described
25 in reference to Figure 4 (step 10). The fabricated discrete electronic devices 80 are separated from each other and the substrate 82 (step 20). A substrate 24 supporting a plurality of column electrodes 22 is provided. The separated discrete electronic devices 80 are provided next to the column electrodes 22 somewhat randomly. The discrete electronic devices 80 can be distributed randomly over the column electrodes 22 such that essentially all of the column electrodes 22 are

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in contact with at least one electronic device 80. Because a dimension of a gap (g2) between adjacent column electrodes 22 is larger than any dimension of a contact surface 81, 83 of each discrete electronic device 80, a single discrete electronic device 80 will contact only one column electrode 22. Multiple discrete electronic devices 80 can be connected to a single column electrode 22. A thickness of the layer of electronic devices 80 provided on the column electrode 22 can be prevented from being greater than twice the thickness of each electronic device 80 by removing excess devices 80. In order to bond the discrete electronic devices 80 to the column electrodes 22, the column electrodes 22 can be pre-treated to provide an adhesive surface. Alternatively, an adhesive layer can be provided between the column electrodes 22 and the discrete electronic devices 80. The discrete electronic devices 80 can also be provided in a slurry which includes a binder and the slurry can be provided on the column electrodes 22 as a coating as described in reference to Figure 4.

A substrate 14 supporting an electrode 16, a display media 12 and a plurality of pixel electrodes 18 is provided. The substrate 24 supporting the column electrodes 22 and the discrete electronic devices 80 is bonded to the substrate 14, such that the discrete electronic devices 80 are electrically connected to the pixel electrodes 18. For example, an anisotropically conductive adhesive can be provided between the pixel electrodes 18 and the discrete electronic devices 80 to provide good electrical contact and bonding. A pressure can be applied to bond the pixel electrodes 18 and the electronic devices 80 together. Standard equipment known to those skilled in the art such as vacuum laminators and thermal presses can be used to provide the pressure.

Figures 4 and 5 illustrate methods of providing discrete electronic devices for an electronic display. However, such methods can be used independently from an electronic display and also can be used in other types of devices.

While the invention has been particularly shown and described with reference to specific preferred embodiments, it should be understood by those skilled in the art that various changes in form and detail may be made therein without departing from the spirit and scope of the invention as defined by the appended claims.

What is claimed is:

Claims

1 1. A method of manufacturing a discrete electronic device, the method comprising
2 the steps of:

3 (a) providing a plurality of discrete electronic devices, each device comprising at
4 least one electronic component and at least one contact surface through which an electrical
5 contact can be made with said at least one electronic component;

6 (b) providing a conductor element comprising a surface bearing at least two
7 electrodes spaced from each other by a gap; and

8 (c) distributing said plurality of discrete electronic devices across said surface of said
9 conductor element so that at least some of said contact surfaces of said electronic devices contact
10 said electrodes, all dimensions of each contact surface being smaller than a width of said gap so
11 that no contact surface contacts more than one of said electrodes.

1 2. The method of manufacturing an electronic device of claim 1 wherein step a) comprises
2 providing the plurality of discrete electronic devices on a first substrate, and further comprising
3 transferring the plurality of discrete electronic devices to a second substrate supporting the
4 conductor element.

1 3. The method of manufacturing an electronic device of claim 2 wherein the at least two
2 electrodes comprise at least two pixel electrodes and the second substrate supports a display
3 media and the pixel electrodes provided adjacent the display media, thereby forming a
4 subassembly of an electronic display.

1 4. The method of manufacturing an electronic device of claim 1 wherein the at least two
2 electrodes comprise at least two column electrodes.

1 5. The method of manufacturing the electronic device of claim 1 wherein step a) comprises
2 manufacturing the plurality of discrete electronic devices on a first substrate.

1 6. The method of manufacturing the electronic device of claim 5 wherein step a) comprises
2 a1) providing a semiconductive material; and a2) providing the semiconductive material adjacent
3 a first surface of the first substrate in a pattern, thereby creating the plurality of discrete
4 electronic devices.

1 7. The method of manufacturing the electronic device of claim 5 wherein at least one of the
2 plurality of discrete electronic devices comprises a diode.

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- 1 8. The method of manufacturing the electronic device of claim 5 wherein at least one of the
2 plurality of discrete electronic devices comprises a back-to-back diode.
- 1 9. The method of manufacturing the electronic device of 5 wherein at least one of the
2 plurality of discrete electronic devices comprises a first layer of P-doped semiconductor, a
3 second layer of N-doped semiconductor provided next to the first layer, and a third layer of P-
4 doped semiconductor provided next to the second layer.
- 1 10. The method of manufacturing the electronic device of claim 5 wherein at least one of the
2 plurality of discrete electronic devices comprises a first layer of N-doped semiconductor, a
3 second layer of P-doped semiconductor provided next to the first layer, and a third layer of N-
4 doped semiconductor provided next to the second layer.
- 1 11. The method of manufacturing the electronic device of claim 5 wherein at least one of the
2 plurality of discrete electronic devices comprises a varistor.
- 1 12. The method of manufacturing the electronic device of claim 5 wherein each of the
2 plurality of discrete electronic devices comprises a two terminal display.
- 1 13. The method of manufacturing the electronic device of claim 1 wherein the at least one
2 contact surface comprises a first contact surface on a first surface of each electronic device and a
3 second contact surface on a second surface of the electronic device opposite the first surface in
4 symmetry.
- 1 14. The method of manufacturing the electronic device of 5 wherein each of the plurality of
2 discrete electronic devices comprises a symmetric current-voltage relationship.
- 1 15. The method of manufacturing the electronic device of 5 wherein the first substrate
2 comprises one of a polymer, a glass, and silicon.
- 1 16. The method of manufacturing the electronic device of claim 6 further comprising step a3)
2 separating the plurality of discrete electronic devices from the first substrate.
- 1 17. The method of manufacturing the electronic device of claim 16 wherein step a3)
2 comprises separating the plurality of discrete electronic device from the first substrate by etching.
- 1 18. The method of manufacturing the electronic device of claim 16 further comprising step a4)
2 providing the plurality of discrete electronic devices separated from the first substrate in a slurry,
3 and step c) comprises distributing said plurality of discrete electronic devices across said surface
4 of said conductor elements by providing a coating of the second slurry adjacent the surface of the
5 conductor element.

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- 1 19. The method of manufacturing the electronic device of claim 18 wherein step c) comprises
2 providing a coating of the slurry having a thickness less than twice the thickness of each discrete
3 electronic device.
- 1 20. The method of manufacturing the electronic device of claim 18 wherein the slurry further
2 comprises a plurality of conductive particles.
- 1 21. The method of manufacturing the electronic device of claim 20 wherein the conductive
2 particles comprises a plurality of gold spheres.
- 1 22. The method of manufacturing the electronic device of claim 18 wherein the slurry further
2 comprises at least one of an adhesive, a viscosity modifier, a surfactant, a corrosion inhibitor, and
3 a polymer.
- 1 23. The method of manufacturing the electronic device of claim 1 further comprising step d)
2 applying a pressure to the plurality of discrete electronic devices and the conductor element to
3 provide good contact.
- 1 24. The method of manufacturing the electronic device of claim 18 wherein the slurry
2 comprises a polymer and further comprising step d) applying heat to reduce viscosity of the
3 polymer in the slurry and applying a pressure to the plurality of discrete electronic devices and
4 the conductor element to provide good contact.
- 1 25. The method of manufacturing the electronic device of claim 18 wherein step a) comprises
2 printing the slurry adjacent the conductor element.
- 1 26. The method of manufacturing the electronic device of claim 3 wherein the display media
2 comprises a plurality of microcapsules.
- 1 27. The method of manufacturing the electronic device of claim 26 wherein each microcapsule
2 comprises one of a plurality of liquid crystals, electrophoretic particles and a bichromal sphere.
- 1 28. An electronic device manufactured using the method of claim 1.
- 1 29. An electronic device manufactured using the method of claim 26.
- 1 30. An electrode assembly comprising:
2 a first conductor element comprising a surface bearing at least two first electrodes spaced
3 from each other by a first gap;
4 a second conductor element spaced from said surface of said first conductor element, said
5 second conductor element comprising a surface bearing at least two second electrodes spaced
6 from each other by a second gap; and

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7 a plurality of discrete electronic devices, each electronic device comprising at least one
8 electronic component and, on opposed sides thereof, first and second contact surfaces through
9 which an electrical contact can be made with said at least one electronic component, said first
10 contact surface of each discrete electronic device being in contact with said surface of said first
11 conductor element, and said second contact surface of each discrete electronic device being in
12 contact with said surface of said second conductor element, the dimensions of said first and
13 second contact surfaces being smaller than a width of said first gap and a width of said second
14 gap so that no contact surface contacts more than one of said first electrodes on said first
15 conductor element and more than one of said second electrodes on said second conductor
16 element,

17 said plurality of discrete electronic devices being substantially randomly distributed over
18 said surfaces of said first and second conductor elements at a density such that essentially all of
19 said first and second electrodes are in contact with at least one of said discrete electronic devices.

1 31. The electrode assembly of claim 30 wherein the first conductor comprises at least two
2 pixel electrodes and the second conductor comprises at least two of column electrodes.

1 32. The electrode assembly of claim 30 wherein the plurality of discrete electronic devices
2 comprises two terminal devices.

1 33. The electrode assembly of claim 32 wherein the plurality of discrete electronic devices
2 comprises back-to-back diodes.

1 34. An electronic display comprising:

2 a display media;

3 a first conductor element comprising a surface bearing at least two pixel electrodes
4 spaced from each other by a first gap;

5 a second conductor element spaced from said surface of said first conductor element, said
6 second conductor element comprising a surface bearing at least two column electrodes spaced
7 from each other by a second gap; and

8 a plurality of discrete electronic devices, each electronic device comprising at least one
9 electronic component and, on opposed sides thereof, first and second contact surfaces through
10 which an electrical contact can be made with said at least one electronic component, said first
11 contact surface of each discrete electronic device being in contact with said surface of said first
12 conductor element, and said second contact surface of each discrete electronic device being in

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13 contact with said surface of said second conductor element, the dimensions of said first and
14 second contact surfaces being smaller than a width of said first gap and a width of said second
15 gap so that no contact surface contacts more than one of the pixel electrodes and more than one
16 of the column electrodes,

17 said plurality of discrete electronic devices being substantially randomly distributed over
18 said surfaces of said first and second conductor elements at a density such that essentially all of
19 said pixel electrodes and said column electrodes are in contact with at least one of said discrete
20 electronic devices.

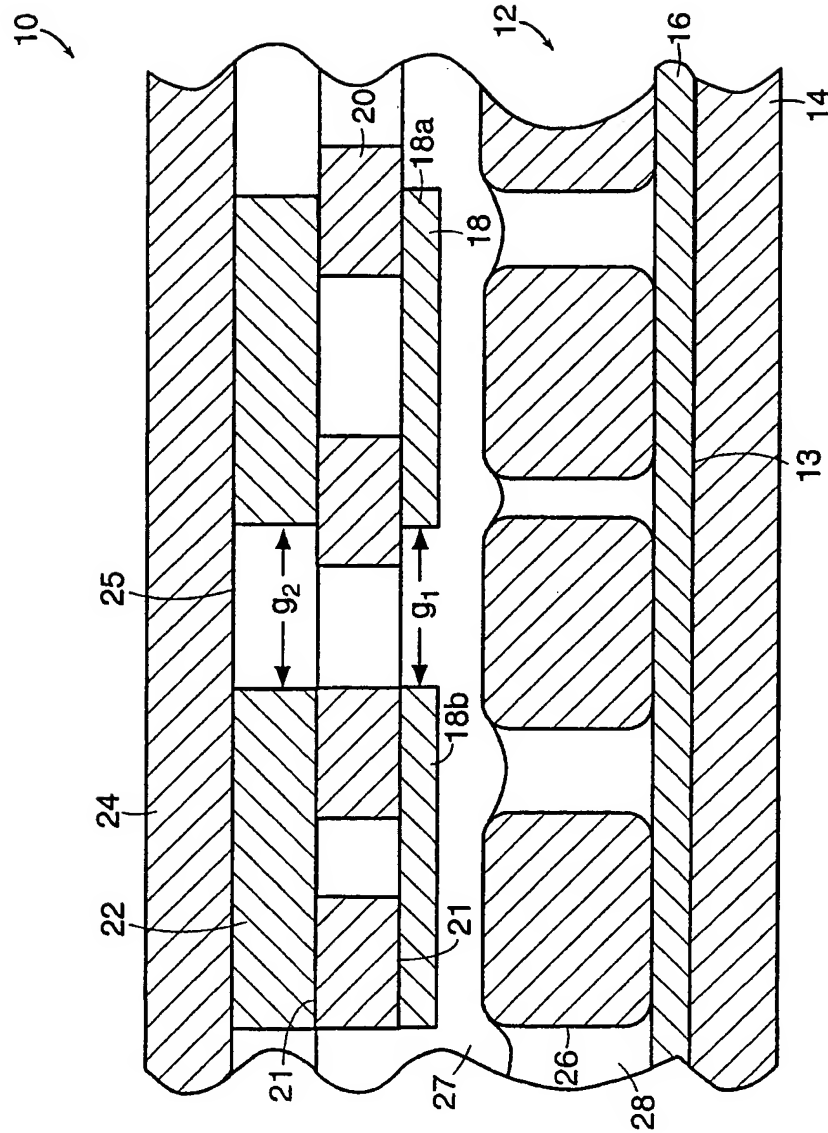


FIG. 1

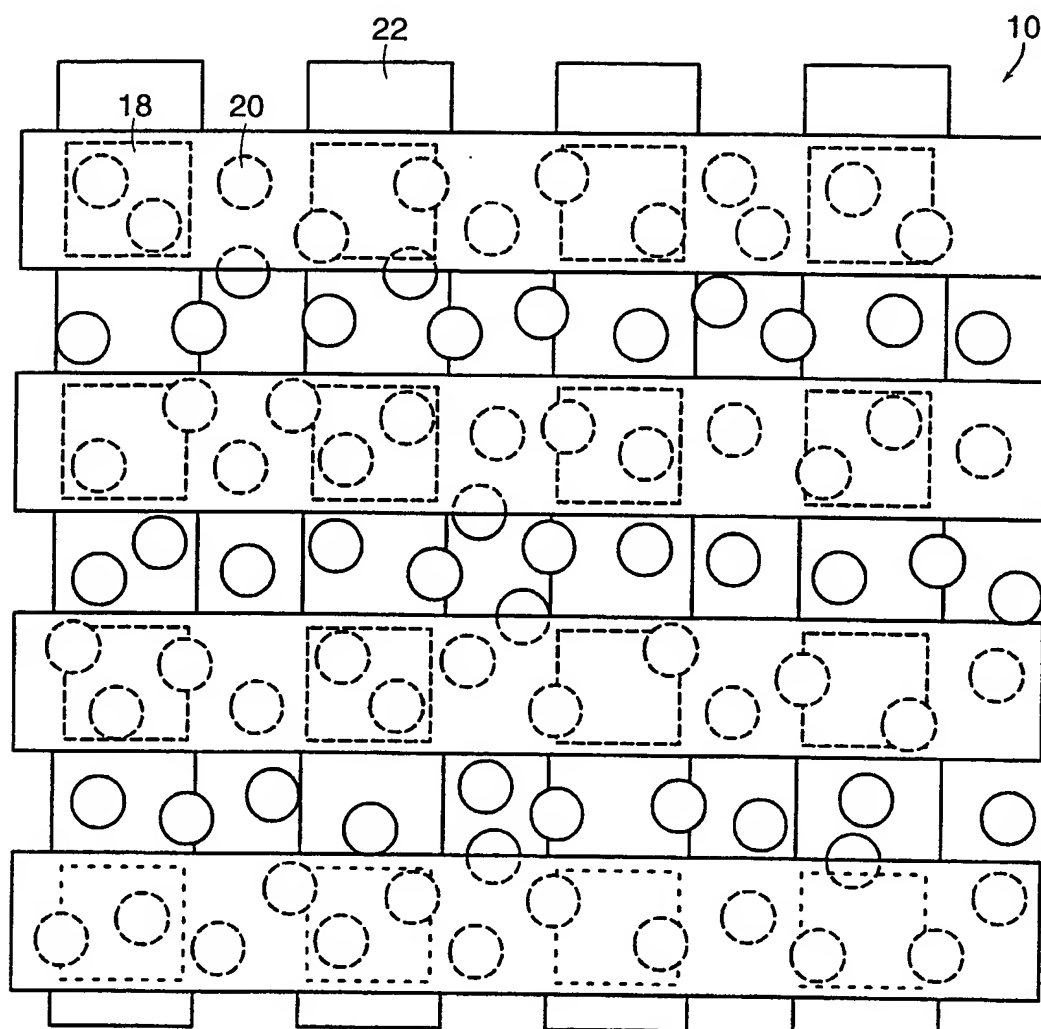


FIG. 2

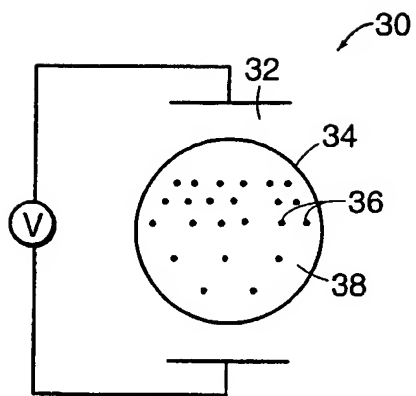


FIG. 3a

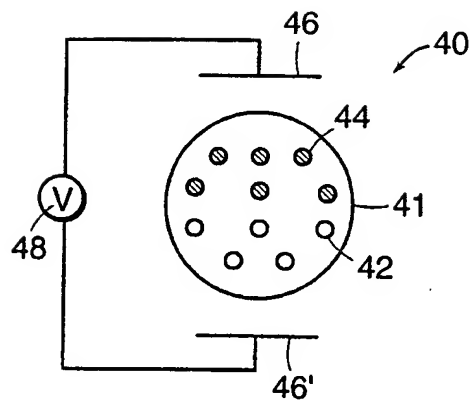


FIG. 3b

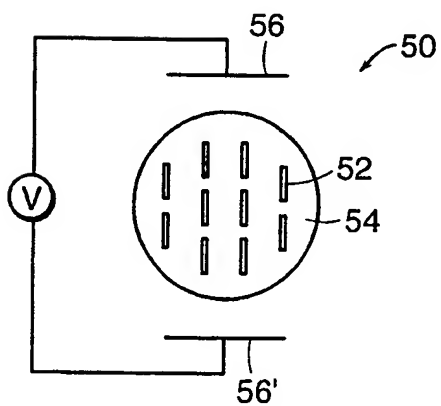


FIG. 3c

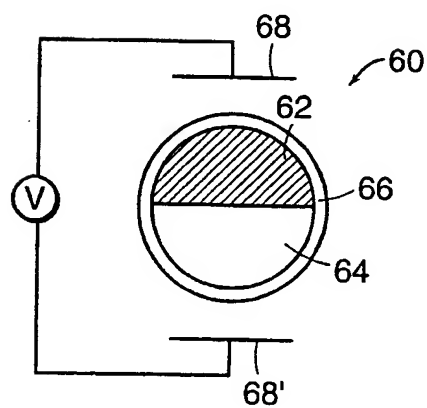


FIG. 3d

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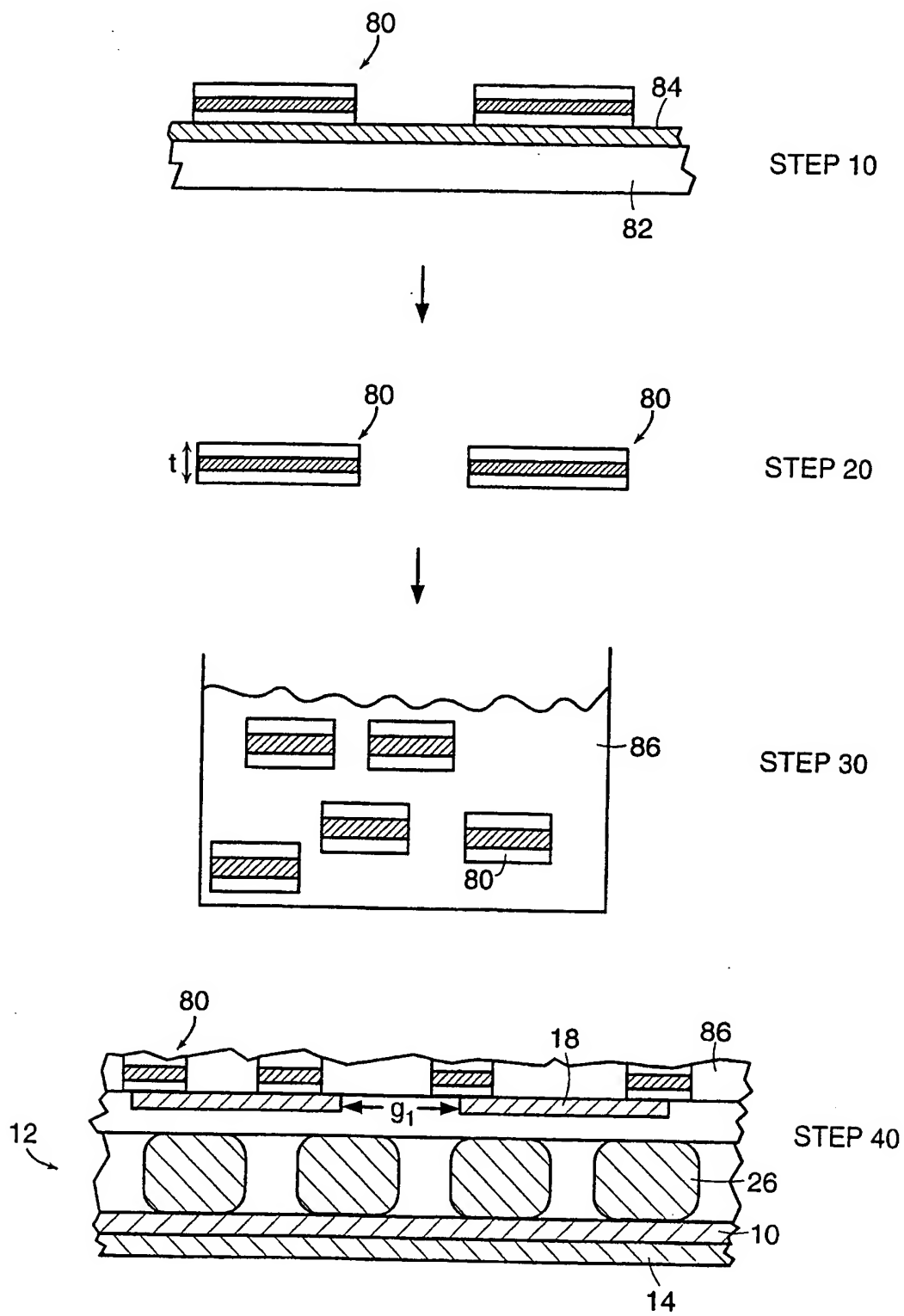


FIG. 4

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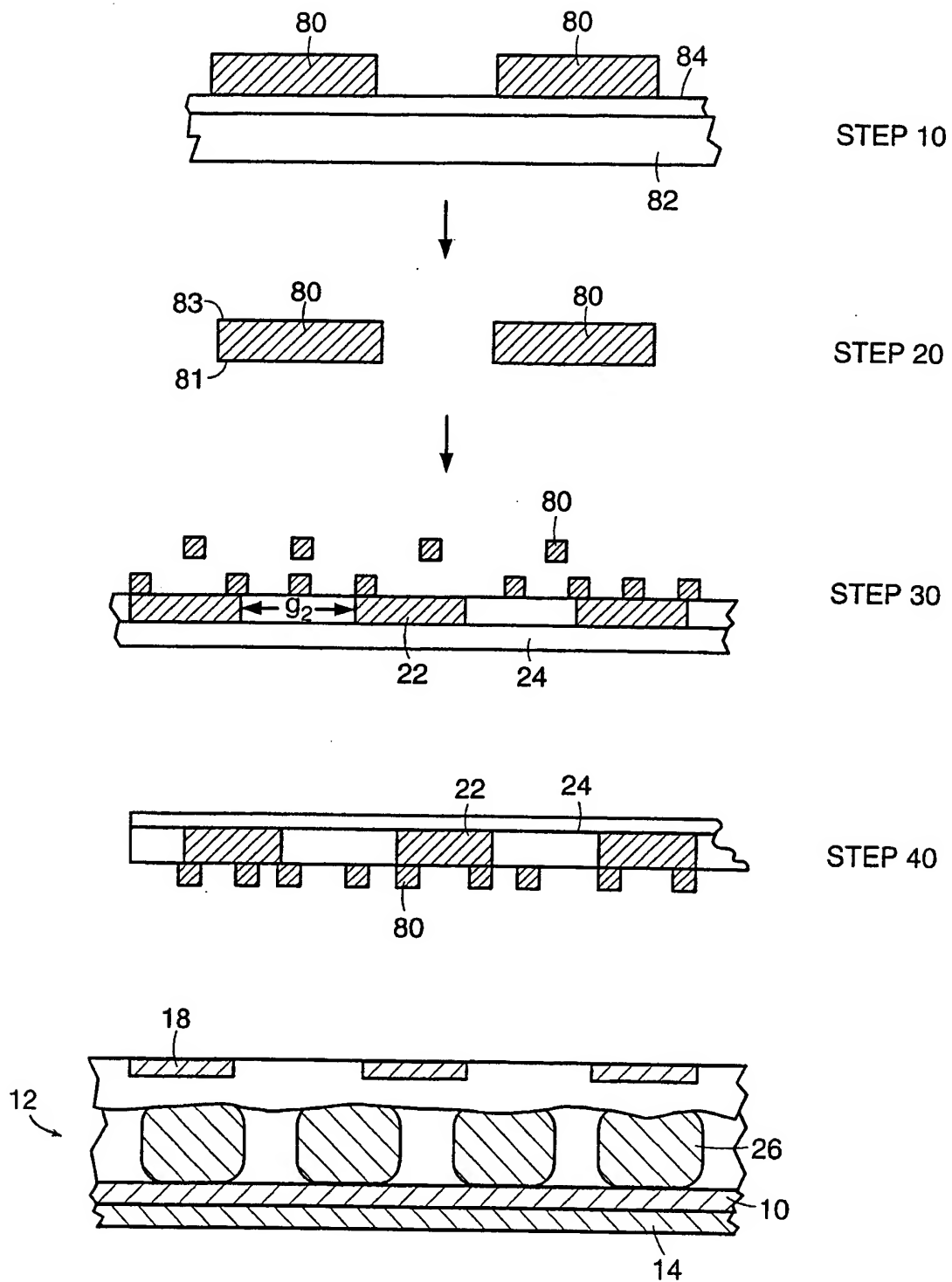


FIG. 5

INTERNATIONAL SEARCH REPORT

Inter. nat. Application No

PCT/US 99/30517

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 G02F1/1365 H01L21/78

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 G02F H01L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 715 026 A (SHANNON JOHN M) 3 February 1998 (1998-02-03) abstract; figures 2,3 column 4, line 12 - line 13 column 5, line 14 - line 26 column 7, line 7 - line 8 column 11, line 27 - line 31	1-34
A	WO 96 41372 A (UNIV CALIFORNIA) 19 December 1996 (1996-12-19) abstract page 1, line 28	1, 30, 34
A	US 5 362 671 A (MCCLELLAND ROBERT ET AL) 8 November 1994 (1994-11-08) cited in the application abstract	1, 30, 34

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Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

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Date of the actual completion of the international search

25 April 2000

Date of mailing of the international search report

03/05/2000

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INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 99/30517

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>DRZAIC P ET AL: "44.31: A PRINTED AND ROLLABLE BISTABLE ELECTRONIC DISPLAY" SID INTERNATIONAL SYMPOSIUM DIGEST OF TECHNICAL PAPERS, US, SANTA ANA, CA: SID, vol. 29, 1998, XP002127322 ISSN: 0098-966X figure 3</p>	26,27

INTERNATIONAL SEARCH REPORT

information on patent family members

International Application No

PCT/US 99/30517

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5715026 A	03-02-1998	GB 2236424 A DE 69018547 D DE 69018547 T EP 0417852 A JP 3131824 A	03-04-1991 18-05-1995 02-11-1995 20-03-1991 05-06-1991
WO 9641372 A	19-12-1996	US 5904545 A AU 5873296 A	18-05-1999 30-12-1996
US 5362671 A	08-11-1994	US 5206749 A US 5528397 A US 5736768 A EP 0565588 A JP 6504139 T US 5396304 A WO 9212453 A US 5376979 A US 5751261 A US 5377031 A US 5539550 A US 5438241 A US 5475514 A US 5666175 A US 5713652 A US 5702963 A US 5583335 A US 5581385 A US 5499124 A US 6043800 A US 5743614 A US 5757445 A US 5661371 A US 5258320 A US 5317236 A US 5258325 A US 5317436 A US 5376561 A US 5444557 A US 5256562 A US 5861929 A US 5331149 A	27-04-1993 18-06-1996 07-04-1998 20-10-1993 12-05-1994 07-03-1995 23-07-1992 27-12-1994 12-05-1998 27-12-1994 23-07-1996 01-08-1995 12-12-1995 09-09-1997 03-02-1998 30-12-1997 10-12-1996 03-12-1996 12-03-1996 28-03-2000 28-04-1998 26-05-1998 26-08-1997 02-11-1993 31-05-1994 02-11-1993 31-05-1994 27-12-1994 22-08-1995 26-10-1993 19-01-1999 19-07-1994